# PATENT ABSTRACTS OF JAPAN

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(71)Applicant: MITSUBISHI PAPER MILLS LTD

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(72)Inventor: SUZUKI KUNIO

ISHIYAMA TAKEYUKI

### (54) COATED PAPER FOR PRINTING

### (57)Abstract:

PURPOSE: To obtain coated paper for printing, producible by high-speed blade coating under good coating conditions and having a high printing gloss and good inking properties.

CONSTITUTION: This coated paper for printing is obtained by oxidizing, modifying and simultaneously gelatinizing an acetylated starch having 0.03-0.1, preferably 0.04-0.1 substitution degree, preferably an acetylated tapioca starch preferably with ammonium persulfate, providing a starch sizing liquid having 15-100mPa.s viscosity under conditions of 35% solid concentration and 60°C, blending the resultant starch sizing liquid in an amount of 3-12wt.% based on the whole solid content in the whole coating liquid therewith, applying the prepared coating liquid onto a substrate and drying the coated substrate. Thereby, high-speed coating suitability due to the higher concentration and improvement in water holding properties is obtained by modifying the acetylated starch with the ammonium persulfate in an autologous modifying process (an oxidizing, modifying and simultaneous gelatinizing process), reducing the viscosity and blending the obtained starch sizing liquid as an adhesive for the coating liquid therein. Furthermore, good inking properties and a high printing gloss are obtained by the higher concentration of the coating liquid.

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#### **CLAIMS**

### [Claim(s)]

[Claim 1] Coated paper for printing with which the viscosity of 35% of solid content concentration comes to blend this pasty liquid of 15 - 100 mPa-s (60 degrees C) three to 12% of the weight into application liquid total solids, and is characterized by being coating and the thing which it comes to dry at a base material using this application liquid by the pasty liquid which comes to become a paste in the formation of oxidation denaturation, and coincidence in the acetylation starch of 0.03-0.1 whenever [permutation].

[Claim 2] Coated paper for printing according to claim 1 with which acetylation starch is characterized by carrying out oxidation denaturation using ammonium persulfate.

[Claim 3] Coated paper for printing according to claim 1 or 2 with which acetylation starch is characterized by being acetylation tapioca.

[Claim 4] Claims 1-3 to which acetylation starch is characterized by being 0.04-0.1 whenever permutation ] are coated paper for printing of a publication either.

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#### **DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[Industrial Application] This invention relates to the new coated paper for printing. The coated paper for printing concerning this invention makes it possible to depend on high-speed blade coating in the state of high-speed coating and especially good coating, and to manufacture, and is related with the coated paper for printing with the outstanding offset-printing fitness, especially high printing gloss, and still better impression nature.

[0002]

[Description of the Prior Art] In recent years, the need over the coated paper for printing with sufficient image quality grows remarkably, with progress of the visualization of printed matter, the impression nature of ink is good and can be equal to high-speed offset printing, the gloss of the printing section is high and the coated paper for printing excellent in the repeatability of a color picture is called for. Moreover, producing the coated paper for printing efficiently is called for with need increase of this coated paper for printing. For this reason, the high-speed coating in a coater, especially a blade coating machine is called for.

[0003] Generally, the coated layer of coated paper is formed by carrying out coating of the application liquid which uses adhesives, a kaolin, and calcium carbonates, such as starch and a synthetic macromolecule latex, as a main pigment. In order to perform high-speed coating by the blade coating machine, generally the method of reducing the concentration of application liquid and increasing a fluidity is taken, but when reducing the concentration of application liquid, offset-printing fitness, such as impression nature, falls remarkably. That is, it is necessary to carry out high-speed coating of the application liquid high-concentration-ized rather from the point of a printability. Then, in order to fill these demands and to give especially high-speed coating fitness, the whiting which carried out wet grinding is used for a pigment, and the technique of improving the fluidity of application liquid is taken (see JP,55-62296,A etc.).

[0004] However, it is not a desirable direction from reducing the gloss of coated paper and worsening impression nature to use wet-grinding whiting abundantly. Moreover, although the technique of improving the high-speed fluidity of application liquid by using the kaolin of a particle, and making possible high-speed coating of high concentration application liquid is also used, if a particle kaolin is used abundantly, the permeability of an ink vehicle will increase and printing gloss will fall remarkably (see JP,59-30992,A etc.).

[0005] Moreover, although there are also coating fitness and a view which raises printing quality while making the starch in adhesives into low-molecular starch, such as cold-water soluble starch and a dextrin, and attaining high concentration-ization, when low-molecular (see JP,58-169595,A etc.) starch is used, the uneven migration of starch tends to happen and it is easy to generate impression nonuniformity.

[0006] Moreover, the process which performs oxidation depolymerize denaturation and formation of a paste of raw starch to coincidence is also introduced for the increase in efficiency of an application

liquid production process. However, although the preservation stability of starch paste liquid was low, the amylose crystallized, the degraded phenomenon which generates precipitation etc. tended to happen and various kinds of antioxidants were examined, there is nothing with decisive effectiveness (see JP,62-240336,A etc.), and high-concentration application liquid cannot be built. [0007]

[Problem(s) to be Solved by the Invention] It is obtaining the coated paper for printing which the purpose of this invention has high offset-printing fitness, especially good impression nature, and high printing gloss in view of this present condition, and can acquire good coating fitness, especially the coating fitness in which high-speed coating's is possible at a blade coating machine with the application liquid of high concentration.

[8000]

[Means for Solving the Problem] The coated paper for printing of this invention is the pasty liquid which comes to become a paste in the formation of oxidation denaturation, and coincidence in the acetylation starch of 0.03-0.1 whenever [permutation], and the viscosity of 35% of solid content concentration comes to blend this pasty liquid of 15 - 100 mPa-s (60 degrees C) three to 12% of the weight into application liquid total solids, and is characterized by being coating and the thing which it comes to dry at a base material using this application liquid.

[0009] The coated paper for printing of this invention is characterized by acetylation starch carrying out oxidation denaturation using ammonium persulfate.

[0010] Moreover, acetylation starch is characterized by being acetylation tapioca.

[0011] Furthermore, acetylation starch is characterized by being 0.04-0.1 whenever [permutation].

[0012] Hereafter, the coated paper for printing of this invention is explained to a detail.

[0013] Whenever [ esterification / of a starch derivative ], whenever [ permutation ] (DS, Degree of Substitution) expresses whenever [ etherification ], and is the average of the permutation hydroxyl group per glucose residue. If it is one permutation, it will become 100 glucoses with 0.01 whenever [ permutation ] (a starch science handbook, Asakura Publishing).

[0014] The approach of carrying out oxidation denaturation, using ammonium persulfate as the oxidation denaturation approach is desirable from the point that viscosity control can be performed easily. Moreover, although raw materials, such as a cone, \*\*\*\*\* starch, and rice, are used for acetylation starch, it is possible, but acetylation tapioca is desirable, in order to raise the stability of starch paste liquid and to obtain high-concentration application liquid. Although whenever [permutation / of acetylation starch] needs to be 0.03 or more, if it is 0.04 or more and 0.1 or less, a still much more good result can be obtained.

[0015] Since it will become the cause of poor impression if molecular weight of a dextrin is remarkable and it is low, although carried out using a dextrin etc. like previous statement in the approach of carrying out depolymerize of the starch in order to raise the fluidity of application liquid, and reducing viscosity, and the water retention of application liquid also falls, it is easy to generate a coating defect, such as a streak and a scratch, under high concentration and it low-concentration-izes, and it becomes low [ the pressure to a blade 1, coating becomes difficult. The cause of these problems is in the point which cannot control freely molecular weight, such as a dextrin, and pasty liquid viscosity under high concentration. [0016] Although the acetylation starch of this invention is processed in the process (it abbreviates to a "private denaturation process" below.) which becomes a paste in the formation of oxidation denaturation, and coincidence, it can perform accommodation of starch molecular weight and viscosity freely by depolymerize and formation of a paste being performed to coincidence in the liquid phase. [0017] Acetylation starch stops being able to age easily compared with non-denaturalized starch, and its stability of pasty liquid increases. Moreover, the water retention of application liquid also improves. This is considered for raising the viscosity (B mold viscosity) in low SHIEA in the condition of a water solution while the recrystallization nature in the inside of the aqueous phase falls, since a part of hydroxyl group of an amylose is blocked. However, although the viscosity (B mold viscosity) in low SHIEA rises, since the viscosity (HSV) in high SHIEA which carries out a bad influence to blade coating-machine operability, such as a streak and a scratch, does not rise, it can secure good water

retention and high-speed blade coating-machine operability. Less than by 0.03, whenever [permutation / of acetylation] is ineffective and demonstrates effectiveness desirable and good at 0.04 or more. Moreover, or more by 0.1, since hydrophobing progresses too much and problems, such as a fall of coated layer reinforcement, are caused on the contrary, it cannot use.

[0018] Since a fluidity increases, the operability of a coating machine is also improved and high concentration-ization is also attained the more the more depolymerize of the starch is carried out in case it blends with application liquid by using the acetylation starch paste liquid of this invention as a binder, impression nature, printing gloss, etc. are improved. It combines, and the preservation stability over aging of acetylation starch paste liquid improves, so that depolymerize of the acetylation starch is carried out by oxidation denaturation.

[0019] It is reducing pasty liquid viscosity with a solid content concentration of 35% to 100 or less mPas under a 60-degree C condition, and, specifically, the high-speed coating in the concentration of 63% or more of application liquid-solid form part concentration becomes possible. However, under a 60-degree C condition, while the workability of a coating machine will get worse by the fall of extreme water retention, migration with still more uneven starch will tend to happen, if molecular weight is reduced to less than 15 mPa-s, impression nonuniformity tends to generate pasty liquid viscosity with a solid content concentration of 35% and it comes to become, the fall of coated layer reinforcement is caused, and a printability falls.

[0020] In case it blends with application liquid by using the acetylation starch paste liquid of this invention as a binder, not only the operability at the time of coating falls, but at less than 3 % of the weight, the water retention of application liquid falls [ the loadings of pasty liquid ] into total solids, and the printing gloss of coated paper falls. On the other hand, when it blends mostly exceeding 12 % of the weight, impression nature tends to fall and a printability is spoiled.

[0022] Among such technique, the thermochemistry degeneration method using persulfate is most excellent in a molecular weight controllability, and is high. [of the viscosity stability of the application liquid at the time of combination in application liquid ] As persulfate, although potassium persulfate, ammonium persulfate, etc. are mentioned for example, ammonium persulfate is desirable in respect of a molecular weight controllability.

[0023] As other adhesives used by this invention, a styrene butadiene system, styrene acrylic, A vinyl acetate system and acrylic, ethylene and a vinyl acetate system, a butadiene methyl methacrylic system, Various copolymers and polyvinyl alcohol, such as a vinyl acetate butyl acrylate system, A maleic anhydride and a styrene copolymer, isobutene and a maleic-anhydride copolymer, Synthetic binders, such as an acrylic acid and a methyl methacrylate system copolymer, The binder generally [ natural system binders, such as oxidized starch, etherification starch, esterification starch, cold-water soluble starch obtained by carrying out flash plate dry cleaning of enzyme denaturation starch or them, casein, and soybean protein, etc. ] known is mentioned. Moreover, various assistants usually used, such as a dispersant, a thickener, a water retention agent, a defoaming agent, a deck-watertight-luminaire-ized agent, and a coloring agent, can use it suitably if needed.

[0024] Moreover, as a pigment for coated paper used by this invention, a preferential grinding object with a kaolin, precipitated calcium carbonate, whiting, wet-grinding whiting, whiting, talc or precipitated calcium carbonate, an aluminum hydroxide, a kaolin, a satin white, etc., clay, a satin white, talc, titanium oxide, an aluminum hydroxide, a silica, a baking kaolin, a zinc oxide, the activated clay, the acid clay, silicon soil, a lake, a plastics pigment, etc. are mentioned.

[0025] The stencil paper used for this invention is milled with acidity, neutrality, and alkalinity including various additives, such as various kinds of loading materials, such as precipitated calcium

carbonate, whiting, talc, clay, and a kaolin, a sizing compound, a fixing agent, a yield agent, a cationized agent, and a paper reinforcing agent, including pulp, such as recycled pulp, such as mechanical pulp, such as chemical pulp, such as LBKP and NBKP, GP, PGW, RMP and TMP, CTMP, and CMP, corrosion gage point, and DIP.

[0026] The stencil paper by which size press was carried out with no size press stencil paper, starch, polyvinyl alcohol, etc. is used for the stencil paper of this invention.

[0027] Moreover, it is also possible to perform double coating to such stencil paper, using the paper which carried out coating of the under coat coating layer by various blade coating machines, a roll coater, the air knife coater, the bar coating machine, the rod blade coating machine, the short DOUERU coating machine, etc. as stencil paper.

[0028] Although the various common coaters of the approach of carrying out coating of the application constituent by this invention to a base paper are usable, and application to a high-speed blade coating machine is mainly considered especially, especially the class of blade coating machine is not limited, and is usable in various blade coating machines, such as a short DOUERU coating machine, a roll applicator mold, and a nozzle applicator mold, and coating is possible for it also in a bevel method and a vent method. A supercalender, gloss calender, software calender processing, etc. are performed to coating and the dried coated paper in this way.

[Example] Although the effectiveness of this invention is further explained to a detail below using an example, thereby, this invention is not limited. In addition, "%" in an example and the "section" show "% of the weight" and the "weight section", respectively. In addition, many measured value in an example is obtained by the following approach.

[0030] 1) The viscosity of pasty liquid measures the temperature of 60 degrees C, the conditions of 60rpm, and the viscosity of application liquid on condition that the temperature of 25 degrees C, and 60rpm using the B mold viscosity mPa-sB mold viscometer of pasty liquid and application liquid. [0031] 2) Measure on condition that the temperature of 25 degrees C, and 1000rpm using the rheometer made from high SHIEA viscosity (HSV) mPa-s Japan Rheology Device (NRM 100-0) of application liquid.

[0032] 3) According to the blank paper glossiness JISP8142, it measured at 75 include angles. (Unit: %) 4) The color overlapping printing glossiness sample was printed with the Roland offset press, it was left at the room temperature one whole day and night, and gloss was measured at the include angle of 60 degrees about the black of a sample, a Magenta, cyanogen, and 4 color pile printing solid printing section of yellow. (Unit: %)

[0033] 5) It printed in IPI ink using the pick on-the-strength RI printing machine (Akira Seisakusho), and the visual judgment of extent of a picking of a printing side was carried out. It is a level with most sufficient 5 by five-step evaluation. A tolerance limit is a rank 3.

[0034] 6) After making water adhere to a test piece using a water absorption impression nature RI printing machine (\*\*\*\*\*\*\*), commercial offset ink was printed immediately and the visual judgment of impression extent was carried out. It is a level with most sufficient 5 by five-step evaluation. [0035] 7) It had the value of B mold viscosity of water retention application liquid, and considered as the index of water retention. Water retention is so high that viscosity is high.

[0036] 8) After carrying out day neglect of the rate pasty liquid of precipitation at the temperature of 60 degrees C, centrifugal separation (3000rpm, 10 minutes) was diluted and carried out to 4% of concentration, and settlings were collected, it dried, and weight was measured. It considered as the rate of precipitation with the rate of settlings to pasty liquid solid content. Settlings are a part for the condensed amylose and were made into the index of stability to aging of pasty liquid with the rate of precipitation.

[0037] Examples 1-6, examples 4 [1-] LBKP of a comparison <stencil paper combination> (\*\*\*\*\*\* 440mlcsf) 70 section NBKP (\*\*\*\*\* 490mlcsf) The 30 sections [0038]

<Internal chemical> calcium carbonate (it displays with \* Hara Kaminaka ash content.) \*6 section marketing cation starch 2 section marketing cation system polyacrylamide yield improver The 0.02

sections [0039] Pulp and an internal chemical were prepared by the above-mentioned combination, and the stencil paper of the basis weight (bone dry) of 50 g/m2 was milled. To this stencil paper, the starch of 0.25 g/m2 was adhered by size press, and the stencil paper for coating was obtained. [0040] Water was added to the preparation approach of denaturation starch> marketing acetylation tapioca starch, or the manufacturer specimen so that solid content concentration might become 35%, and starch suspension was prepared. Ammonium persulfate was added to this, by SEPIKUKKA (product made from Japanese Food processing), while carrying out oxidation denaturation under the vapor pressure of 7kg, the temperature of 145 degrees C, and the conditions for holding-time 5 minutes, after becoming a paste, the sodium-hydroxide solution was added, it neutralized and preparation of

[0041] The denaturation starch obtained by the approach of which the adjustment approach of application liquid and the <coating approach> above were done was used, and application liquid of 63% of solid content concentration was prepared according to the following loadings.

[0042]

application liquid was presented with this. The amount of ammonium persulfate adjusted starch paste

(Application liquid combination)

liquid viscosity.

The 1st class kaolin of marketing (ultra White 90) The 2nd class kaolin of 30 section marketing (ultra coat) 40 section marketing wet whiting (Karr Vital 90) 30 section marketing polyacrylic acid system dispersant 0.1 section denaturation starch 6 section marketing styrene butadiene latex (JSR0617) 8 section calcium stearate 0.3 section sodium oxide The 0.15 sections [0043] It is the above-mentioned application liquid at the rate of 800 m/min to the above-mentioned stencil paper for coating by the hula dead nip mold blade coating machine (Mitsubishi Heavy Industries, LTD. make) One side 10 g/m2 Coating was carried out and it dried. Subsequently, supercalender processing was performed on condition that linear pressure 220 kg/cm and rate 300 m/min, and the coated paper for printing was obtained. About the obtained coated paper for printing, after performing gas conditioning within the air conditioned room of 20 degrees C and 65%RH for 24 hours or more, measurement of quality of paper was performed.

[0044] It prepared like the example 1 except having blended the 3 sections of denaturation starch obtained according to the example 7 preparation approach[ of application liquid ], and coating approach> example 1. Coating as well as an example 1 was performed, and obtained the coated paper for printing.

[0045] It prepared like the example 1 except having blended the 11 sections of denaturation starch obtained according to the example 8 <adjustment approach [ of application liquid ], and coating approach example 1. Coating as well as an example 1 was performed, and obtained the coated paper for printing.

[0046] It denaturalized like the example 1, using commercial acetylation cone starch as a raw material of the example 9 preparation approach of denaturation starch> denaturation starch.

[0047] The denaturation starch obtained with the preparation approach of application liquid and the <coating approach> above was used, and it prepared like the example 1. Coating as well as an example 1 was performed, and obtained the coated paper for printing.

[0048] The result of each example was summarized in Tables 1 and 2. In addition, the value of the streak of front Naka shows the number of the streak generated in per 10,000m.

[0049] It prepared like the example 1 except having blended the 2 sections of denaturation starch obtained according to the example 5 preparation approach [ of application liquid ], and coating approach> example 1 of a comparison. Coating as well as an example 1 was performed, and obtained the coated paper for printing.

[0050] It prepared like the example 1 except having blended the 13 sections of denaturation starch obtained according to the example 6 preparation approach [ of application liquid ], and coating approach> example 1 of a comparison. Coating as well as an example 1 was performed, and obtained the coated paper for printing.

[0051] It denaturalized like the example 1, using commercial corn starch as a raw material of the

example of comparison 7 reparation approach of denaturation starch> denaturation starch.
[0052] The denaturation starch obtained with the preparation approach of application liquid and the
<coating approach> above was used, and it prepared like the example 1. Coating as well as an example
1 was performed, and obtained the coated paper for printing.

[0053] Water was added, starch suspension was prepared so that solid content concentration might become the example of comparison 8 preparation approach of starch paste liquid> marketing dextrin with 35%, this was heated at 95 degrees C for 30 minutes, and starch paste liquid was prepared.

[0054] The starch paste liquid obtained with the preparation approach of application liquid and the <coating approach> above was used, and it prepared like the example 1. Coating as well as an example 1 was performed, and obtained the coated paper for printing.

[0055] The result of each example of a comparison was summarized in Tables 3 and 4. In addition, the value of the streak of front Naka shows the number of the streak generated in per 10,000m. If the post of an example was taken from Table 1 and Table 2, the good result was obtained also about which property.

[0056]

[Table 1]

9	夷 施 例	1	2	3	4	
	澱粉種	对机化 处 劫	7tfn化 9t <b>动</b>	7 <b>55</b> 化 处 <b>肋</b>	<b>Pt打小t</b> 处 动	
澱	置換度 APS(%) B型粘度	0.03 2.2 40 0.8	0.04 2.3	0.07 2.5 40 0.2 6	0.10 2.8 40 <0.1	
粉	沈海率 % 配合部数	0.8 6	2.3 40 0.5 6	0.2 6	(0.1 6	
塗	B型粘度 HSV	1600 37.6 1.5	1800 43.5	2400 45.1	2800 46.1	
被	ストリーク	1.5	0	0	0	
盟	印刷光沢 着肉性 強度	49.4	49.6	52.0 5 4	52.5 4.5	
質	強度	4 3.5	5 4	4	4.5	

[0057]

[Table 2]

実	施例	5	6	7	8	9
澱	澱粉種	7 <b>t</b> fn/t 5t 动	对机化 处 动	对于小比 外 动	对机化 处 肋	アセチル化コーン
粉	置換度 APS(%) B型率 洗取率 洗配合部数	0.07 3.0 15 <0.1 6	0.07 1.2 100 0.8 6	0.07 2.5 40 0.2 3	0.07 . 2.5 40 0.2 12	0.07 2.7 40 0.9 6
塗被	B型粘度 HSV みリーク	2100 39.0	3600° 72.6	1650 38.4	4000 82.1	2700 46.1
品質	印刷光沢 着肉性 強度	49.2 4.5 3.5	53.2 5 4.5	48.3 4.5 3.5	54.8 4 5	50.1 4.5 4.5

[0058] [Table 3]

H	較 例	1	2	3	4
澱	澱粉種	对机化 外 加	7 <b>tfM</b> 化 5t	7 <b>tfM化</b> 9比 动	7世孔化 5七 动
粉	置換度 APS(%) B型粘度 沈澱率 % 配合部数	0.02 2.1 40 3.0	0.11 3.0 40 <0.1 6	0.07 4.0 10 <0.1 6	0.07 1.1 110 1.2 6
塗被	B型粘度 HSV 사リーケ	1500 31.7 3	3200 52.1 1	600 23.3 多発	4500 98.7 10
品質	印刷光沢 着肉性 強度	48.1 4.5 4	52.3 4 3	46.5 3.5 2.5	52.0 4 5

## [0059]

## [Table 4]

比	較 例	5	6	7	8
澱	澱粉種	对机化 处 加	<b>Ptf</b> x化 <b>9</b> 比 <b>动</b>	コ <del>-</del> ン 及 <del>-チ</del>	デキストリン
粉	置換度 APS(%) B型料度 沈凝率 % 配合部数	0.07 2.5 40 0.2 2	0.07 2.5 40 0.2 13	 1.8 40 5 6	30 6
塗被	B型粘度 HSV ストリーウ	850 32.5 5	4300 90.4 4	650 26.7 10	650 39.3 5
品質	印刷光沢 着肉性 強度	43.1 4.5 2.5	53.9 3.5 5	48.1 4.5 4	51.5 3 3

## [0060]

[Effect of the Invention] As mentioned above, the coated paper for printing which good high-speed coating fitness was acquired by high application liquid concentration by this invention, and was [ like / it is \*\*\*\*\*\* and ] excellent in high offset-printing fitness especially impression nature, and printing gloss can be obtained.

# [Translation done.]